DEVELOPMENT AND CHARACTERIZATION OF MOISTURE-BLOWN NATURAL RUBBER FOAM PREPARED BY MICROWAVE FOAMING TECHNIQUE

By

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LIST OF ABBREVIATIONS

ADC	Azodicarbonamide
ASTM	American Standard Test Methods
CBA	Chemical blowing agent
CBS	N-cyclohexyl-2-benzothiazolesulfenamide
CFC	Chlorofluorocarbon
CR	Chloroprene rubber
EPDM	Ethylene propylene diene rubber
ISM	Industrial, scientific and medical
MU	Mooney unit
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
OBSH	4,4’-oxybis(benzenesulphonylhydrazide)
PBA	Physical blowing agent
pphr	Part per hundred rubber (resin)
PVC	Polyvinyl chloride
PS	Polystyrene
PU	Polyurethane
RF	Radio frequency
SBR	Styrene butadiene rubber
SMR-L	Standard Malaysian Rubber L
TMTD	Tetramethylthiuram disulfide

LIST OF SYMBOLS

^{o}C	Degree Celsius
ρ	Density
ZnO	Zinc oxide
m	Meter
mm	Millimeter
cm	Centimeter
%	Percentage
wt%	Weight percentage
g	Gram
Hz	Hertz
eV	Electronvolt
W	Watt
Pa	Pascal
min	Minute
s	Second
K	Kelvin
J	Joule
mol	Mole

PEMBANGUNAN DAN PENCIRIAN BUSA GETAH ASLI TIUPAN-LEMBAPAN DISEDIAKAN DENGAN TEKNIK PEMBUSAAN GELOMBANG MIKRO

ABSTRAK

Kajian terhadap keupayaan gelombang mikro untuk menghasilkan busa getah asli telah dijalankan. Kajian mendapati bahawa pembusaan gelombang mikro berupaya untuk mengembangkan getah asli dan pemprosesan gelombang mikro mempunyai kelebihan berbanding dengan proses pembusaan berperingkat tunggal dan juga berperingkat dua. Secara semula jadi, getah asli bersifat tidak berkutub dan tidak cenderung terhadap pemanasan gelombang mikro, tetapi kelakuannya di bawah pengaruh gelombang mikro boleh diubahsuai dengan penggabungan pelbagai jenis bahan tambah. Busa dengan ketumpatan relatif serendah 0.14 dapat dihasilkan dengan penambahan 8 bahagian per seratus getah (pphr) azodikarbonamida (ADC) tetapi kesan perosotan boleh diperhatikan apabila kepekatan ADC yang lebih tinggi digunakan. Apa yang lebih menarik adalah kandungan lembapan dalam sebatian getah juga mampu bertindak sebagai suatu ejen pembusaan yang berpotensi dengan bantuan sinaran gelombang mikro. Busa dengan ketumpatan relatif paling rendah daripada penyelidikan ini, iaitu 0.10, dapat dihasilkan dengan memanfaatkan kandungan lembapan sejumlah 1.25% dalam sebatian getah. Kejayaan pembusaan tersebut dapat mengatasi pembusaan sebatian yang dibentuk dengan penambahan 10 pphr azodikarbonamida. Perkara ini diunjurkan mampu merevolusikan industri busa memandangkan air ialah satu bahan yang berkos rendah, mudah didapati dan tidak toksik. Penambahan pengisi, silika ataupun karbon hitam, akan meningkatkan kecenderungan sebatian getah untuk dipanaskan dengan gelombang mikro, tetapi ianya tercapai dengan cara yang berbeza. Silika akan meningkatkan kekutuban sebatian getah manakala karbon hitam

meningkatkan kekonduksian electrik sebatian. Kajian mendapati bahawa penambahan lebih daripada 10 pphr bagi kedua-dua pengisi, berakhir dengan kegagalan dalam penghasilan busa getah asli. Bagi sebatian yang ditambah dengan silika, kelikatan leburan polimer yang tinggi semasa proses pembusaan telah mengehadkan pengembangan matrik getah. Dalam kes karbon hitam pula, kenaikan suhu yang cepat bawah sinaran gelombang mikro telah menyebabkan ada kesan pembakaran dan perosotan pada sebatian getah sebelum struktur busa boleh terbentuk.

DEVELOPMENT AND CHARACTERIZATION OF MOISTURE-BLOWN NATURAL RUBBER FOAM PREPARED BY MICROWAVE FOAMING TECHNIQUE

ABSTRACT

Investigation has been done on the feasibility of utilizing microwave radiation in foaming natural rubber. It was found that microwave foaming was able to foam natural rubber and the microwave processing is having advantages over both single and two-stage foaming process. Natural rubber is naturally non-polar and unsusceptible to microwave heating, but its behavior under the influence of microwave can be modified by incorporation of various additives. Foam with relative density as low as 0.14 can be produced with 8 pphr of azodicarbonamide (ADC) added, however signs of degradation can be observed when higher concentration of ADC was utilized. More interestingly, the moisture content in the rubber compound itself was able to act as a potential physical blowing agent with the aids of microwave radiation. Foam with the lowest relative density from this research, *i.e.* 0.10, was able to be produced by exploiting 1.25% moisture content in rubber compound. The successful foaming with moisture exceeded those foams formed with the addition of 10 pphr of azodicarbonamide. This would revolutionize the foam industry since water is a low cost, abundant and non-toxic material. The addition of fillers, silica and carbon black, will increase the susceptibility of rubber compound towards microwave heating, but in different manners. Silica will increase the polarity of rubber compound while carbon black increases the electrical conductivity of the compound. It was found that the addition of more than 10 pphr of both fillers ended up with unsuccessful production of natural rubber foam. For silica-added compound, the high viscosity of polymer melt available during foaming restricted the expansion of rubber matrix. In the case of carbon black added compound, the rapid

rise in temperature under microwave radiation would burn and degrade the compound before the foam structure can be formed.

INTRODUCTION

1.1 Introduction and Problem Identification

Foam is a unique type of matter which gases or spherical gaseous voids are introduced into a dense medium. This will produce a class of material with high property/weight ratio, which will enhance the versatility of the material used to be foamed. Polymeric material, regardless it is thermoplastic, thermoset or elastomer, is known to have a high property/weight ratio if compare to conventional materials like metal, glass or wood, and due to this property, people is seeking ways to replace conventional materials with polymeric materials in some application where light weight is preferred. Foamed polymer represents an important extension of the polymer properties spectrum and has an enhanced property/weight ratio characteristic, therefore offering some unique advantages (Lee, *et al.*, 2007).

The main advantages of polymeric foam is the energy insulating capability in the form of heat, sound, mechanical or electric energy, and in conjunction of the low density nature, had become significant in different applications and environments (Rosato, *et al.*, 2004). Polymeric foams can be used in applications ranging from original to replacement parts in building, vehicles, sports equipment, boats, spcacrafts, furniture, toys and life preservers. The major polymers commonly transformed into foams are polyurethane (PU) and polystyrene (PS).

One major issue of polymeric materials comes from the raw material for synthesizing polymers. The monomers essentials for polymerization majority come from the cracking of petroleum, which is a non-renewable resource. It has been reported by Fernandez (2006) and Eyerer (2010) that the production of polymers consumed 4% of petroleum worldwide. Ibeh (2011) stated that raw materials for polymers are oil,

natural gas, coal and agricultural products such as corn and soybean, and due to current "green and sustainability" era, the use of agricultural and non-fossil-type raw materials are encouraged. In this sense, natural rubber (NR), which is obtained by processing of latex tapped from *Havea brasiliensis*, suits the criteria of sustainable raw materials and if other synthetic polymer foams can be replaced by NR foam, it will have impact onto the consumption of petroleum by polymer industries.

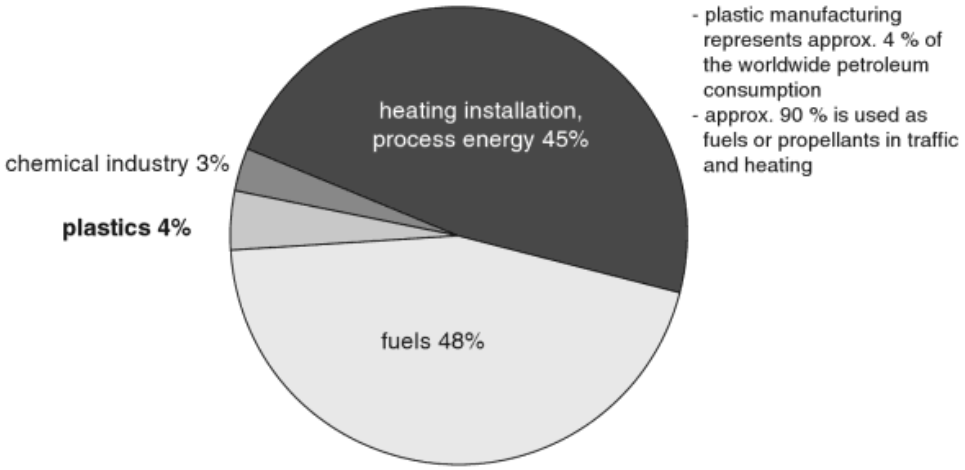

Figure 1.1: Petroleum consumption worldwide (Eyerer, 2010, p.12).

Some research have been done on the production of NR foam (Sombatsompop & Lertkamolsin, 2000; Ariff, *et al.*, 2007; Lee & Choi, 2007; Najib, *et al.*, 2009; 2011). Majority of these researches focused on two-stage foaming of NR foam, where long cycle time around 20 to 30 min is needed to produce one single sample. For single stage foaming, the cycle time varies with the optimum curing time of the rubber itself, obtained from rheometer testing. However, high density foams will be produced if single stage foaming is utilized instead of two-stage foaming. Both processes suffer from their own shortcomings but also hold advantages over one another.

Past research (Tan, 2012) on single stage foaming had been able to produce NR foam with relative density as low as 0.142, but comes with one limitation, the waste of

material. Figure 1.2 shows an NR foam produced by single stage foaming with thick solid skin, considered to as wastage in the production. Rubber compound was completely filled a 1 cm thick mold and the resulting foam was having total of about 3 mm of solid skin, renders the wastage up to 30% of the material. This limitation is brought by the poor heat conduction of rubber during compression molding. Long period of time is needed for the heat to be transferred into the core, but vulcanization had completed at the surface, which makes rubber in the skin area was unable to be foamed.

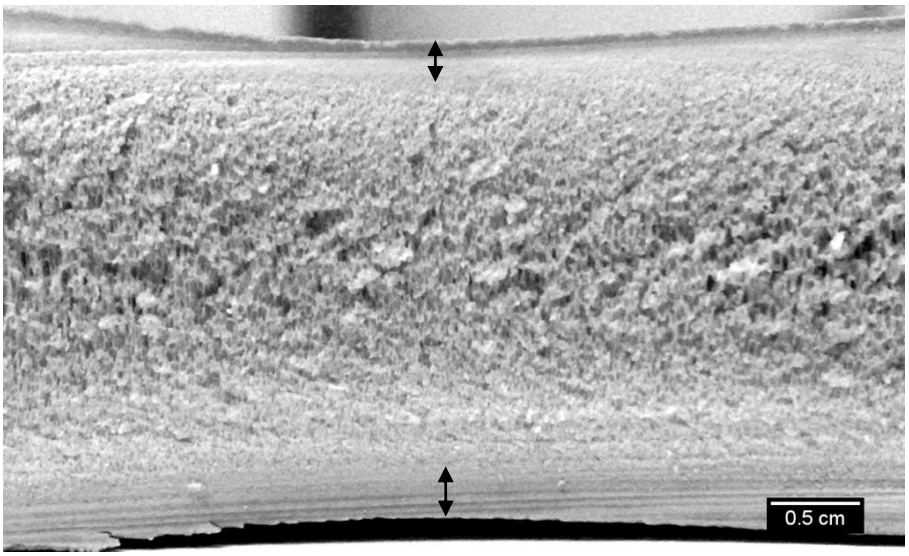

Figure 1.2: Single stage foaming NR foam with thick solid skin (Tan, 2012).

Microwave foaming is a relatively safe process, compared to radiations such as gamma-ray or X-ray. Microwave heating has been utilized in household application which provides uniform heating throughout the material, not only on the surface, but the whole material from the core to the surface. By making use of microwave heating in rubber foaming, it is believed that the rubber compound can be heated uniformly and vulcanization together with foaming can be done simultaneously in the whole volume of the compound. If possible, microwave foaming technique can compete with single stage

foaming on the cycle time and material wastage aspects, and also compete with two-stage foaming on the ease of controlling and low density of foam.

1.2 Objectives

The main objective of this research is to study the feasibility of microwave heating in vulcanizing and foaming of expandable natural rubber (NR) compound. Along with the main objective, some other minor objectives that will be achieved are:

- To evaluate the curing characteristics and behavior of NR compound exposed to microwave radiation.
- To investigate on the concentration of blowing agent towards the properties of resulting foams.
- To study on the effect of moisture content in NR compound and the ability of water to act as a blowing agent in conjunction with microwave foaming technique.
- To investigate the effects of fillers onto the processing of NR foam under microwave foaming technique.

1.3 Scope of Work

Although microwave is used in the processing of rubber foam in this research, the in-depth coverage of microwave fundamentals will be limited since the research is focused on material science. Basic microwave theory will be forwarded and reviewed but attention will be given onto the behavior of rubber compound under the microwave radiation.

Evaluation will be done on the NR foam in terms of crosslink density, relative density, foam morphology and compression strength. The obtained results will then be

related with the parameters chosen and study the influence of each parameters towards the production of NR foam.

LITERATURE REVIEW

2.1 Polymeric Foam

Polymeric foam, or also known by the name expanded polymer, sponge polymer, cellular polymer or structural foam (Rosato, *et al.*, 2004) is a material generally consists of at least two necessary phases, solid polymer matrix phase and gaseous phase created by blowing agent (Okoroafor & Frisch, 1995). The solid polymer phase may be composed of a single polymer, polymer blends based on two or more polymers, homogeneous or heterogeneous (Klempner, 2004), in the form of interpenetrating polymer networks or pseudo-interpenetrating polymer networks (Okoroafor & Frisch, 1995). Other solid phases that may exist would be fillers, in any existing forms and from any possible materials.

Polymeric foams can be flexible, semi-rigid or rigid, which the reason behind its flexibility can be traced back to the glass transition temperature of that particular polymer, whether it is a single polymer, homogeneous or heterogeneous polymer blends. Okoroafor & Frisch (1995) and Klempner (2004) defined the flexibility of foam in room temperature but did not consider the influence of surrounding environment towards the foam itself. The rigidity of polymer foams may also be influenced by the environment it is in as surrounding temperature higher than its glass transition temperature will cause the foam to be flexible and lower surrounding temperature will leave the foam rigid and brittle. In the sense of flexibility, heterogeneous polymer foams may possess both flexible and rigid properties at a given temperature, resulting in higher range of application, but may be susceptible to the issue of compatibility of the polymer blends.

With the technology nowadays, almost any polymer, thermoplastic or thermoset, can be made into cellular form with suitable techniques. There are quite a few methods

that can be chosen to impart gaseous phase into a solid polymeric material and are listed below (Okoroafor & Frisch, 1995; Klempner, 2004):

- Thermal decomposition of chemical blowing agents mixed in the polymer matrix as additive and produces gas, generally nitrogen or carbon dioxide.
- Mechanically whipping air bubbles into the polymer system, which in this case has to be in molten, solution or suspension state, and the air bubbles are entrapped in the polymer matrix hardens.
- Evaporation of low boiling liquids such as chlorofluorocarbon (CFC) by the application of heat.
- Volatilization of gases produced by polymerization such as reaction of isocyanate with water in the case of PU.
- Expansion of dissolved gas in the polymer when the pressure of the system is reduced.
- Incorporation of hollow microspheres into the polymer matrix.

Polymeric foams are used in various applications, mainly due to the insulation property towards mechanical, thermal and acoustical energy. Closed-cell foams are suitable for electrical and thermal insulation while open-cell foams are good for acoustical insulation, having higher moisture absorption capacity and higher permeability to gas (Okoroafor & Frisch, 1995; Shutov, 2004). The division of foams into closed-cell and open-cell is based on the cell geometry. In closed-cell foams, the gas cells are completely enclosed by cell walls, while in open-cell foams, the dispersed gas cells are unconfined and are connected by open passages (Rosato, *et al.*, 2004). Figure 2.1 shows the distinctive morphology of open-cell and closed-cell foams.

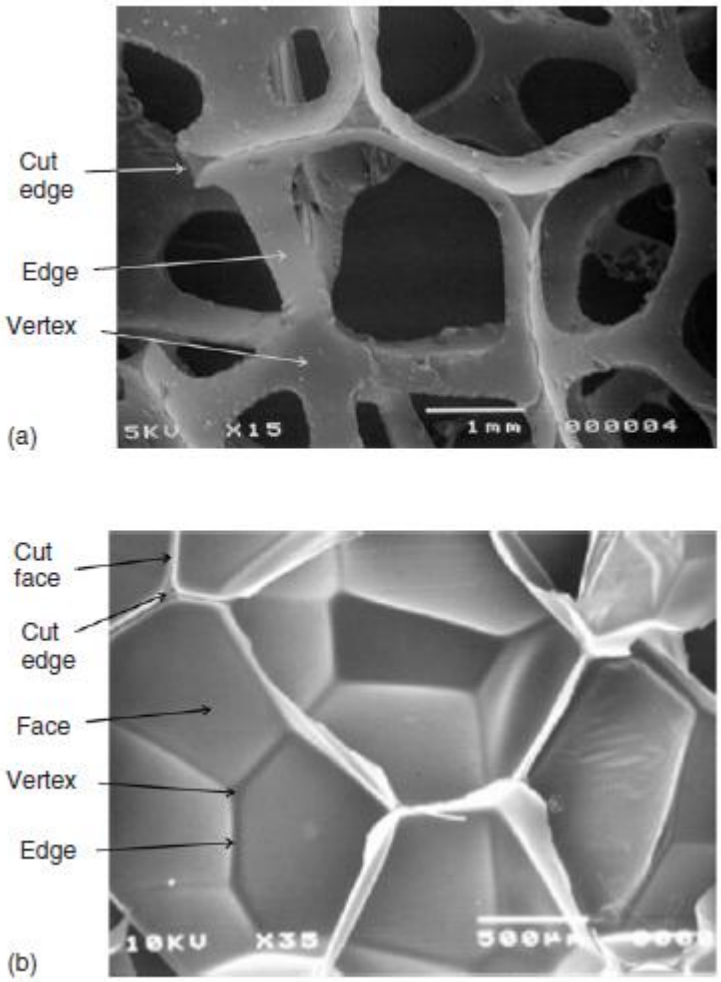

Figure 2.1: Example of (a) open-cell foam and (b) closed-cell foam (Mills, 2007, p.2).

NR is natural *cis*-1,4-polyisoprene which occurs in over 2000 species of higher plants, or called vascular plants. Plants such as *Taraxacum kok-saghyz, Parthenium argentatun, Slidago altissima* and *Dyera retusa* are known to produce *cis*-1,4-polyisoprene, but NR from *Havea brasiliensis*, or commonly just known as rubber tree, remains the most widely used, which accounts for about 40% of the total rubber consumed worldwide (Eng & Ong, 2001). Other types of polyisoprene exist as *trans*-1,4-polyisoprene, or normally named as gutta-percha, but the material is inelastic thermoplastic which softens upon heating and chemically inert (White, 1995). Although the two materials are having the same type of substituent, but the chain configuration across the double bond has tremendous effect on the mechanical properties of the two

materials. Figure 2.2 shows the comparison of chemical structure between NR and gutta-percha.

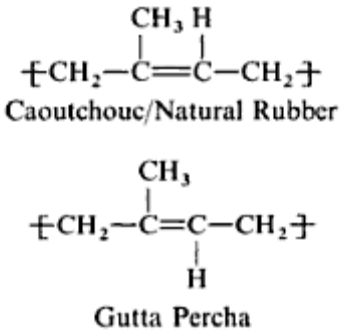

Figure 2.2: Comparison between NR and gutta-percha (White, 1995, p.6).

Previous researchers have been finding methods to produce synthetic polyisoprene which can be used to replace NR in many applications. This however is never been achieved. One of the reasons is that NR is having small amounts of nonisoprene groups, which are known as abnormal groups, present on the main chain molecules. These abnormal groups such as epoxide, ester, aldehyde and lactone, comes in very low concentration, but exert strong influence on the properties of NR (Eng & Ong, 2001). Hence, although synthetic polyisoprene could have up to 99% of rubber hydrocarbon, while NR is usually around 93% of rubber hydrocarbon, it is still incapable of totally replacing NR (Gary, 2001).

NR consists of almost 100% of cis-1,4-polyisoprene, which the stereoregularity of the polymer chains impart the ability to form stress-induced crystallization upon stretching and resulting in high modulus and tensile strength of NR (Eng & Ong, 2001). It is highly resilient and due to the hysteretic properties, NR experiences little heat build during flexing, which makes it a great choice in applications where shock and dynamic load requirements are important (School, 2001). NR has its disadvantages, such as poor resistance to oxidation, heat aging, ozone, weathering, hydrocarbon oils, and

concentrated acids and bases. These problems can normally be overcome by blending NR with synthetic rubbers, or antidegradants can be added as additives.

NR foam can be produced from either of the two forms of NR, raw rubber and latex. Only the production of NR foam using blown dry rubber will be focused in this work. Landrock (1995) states that blown dry rubber and foamed latex are distinctly different materials, but the end products may appear similar and have overlapping applications.

Generally, the word sponge rubber is used to refer to both closed-cell and open-cell rubber foam, but to be more specific, sponge rubber is defined as cellular rubber consisting predominantly of open cells made from a solid rubber compound while expanded rubber is referring to closed-cell rubber foam (Landrock, 1995; Annicelli, 2001).

2.2 Blowing Agents

Blowing agent is considered to be the most important additive to be added into polymer matrix if foams are to be produced, since one of the necessary phases in foam materials is the gaseous phase represented by either closed-cell or open-cell structures. Other than producing foams, blowing agent also can be used in other application, such as 0.1 wt% of blowing agent can be added to eliminate sink marks in injection molded parts (Rosato, *et al.*, 2004). As mentioned previously, various methods can be used to incorporate gaseous phase into polymer matrix, depending on the material to be foamed, and some other reasons should also be considered when choosing the suitable method, such as the ease of processing and safety issue.

Blowing agents can be classified into two groups, physical blowing agents (PBA) and chemical blowing agent (CBA), which is differentiated by the mechanism of gas

liberation by the blowing agents (Shutov & Visco, 2004). PBA produces gas by means of changing in physical state of the PBA itself, such as volatilization of CFC under heat; while CBA liberates gas by chemical means such as thermal decomposition of the CBA or chemical reaction between two reagents to produce gas (Rosato, *et al.*, 2004; Singh, 2004).

Shutov & Visco (2004) criticized the simple classification of blowing agents into two major groups, PBA and CBA. In their opinion, the compounds people used to foam polymers or other materials should first be classified into gases and blowing agents, and secondly the latter is further divided into PBA and CBA. Example has been given based on this classification, where gases mixed into polymer matrix under high pressure, does not undergo any change in physical state when the pressure is reduced and the gas expand to foam the polymer. In this case, the gases used to foam polymer does not fulfill the requirement to be classified into the group of PBA where change in physical state is essential.

Sims & O'Connor (1997) stated that blowing agent system of polymer has undergone significant changes over the past decades due to environmental issue, which virtually eliminated the use of CFC as PBA. The replacement of CFC which was hydrocarbon was having additional potential flammability and explosion hazards not only during processing but also during storage, transportation. For the mentioned reasons, CBA systems had received increased interest from researchers and manufacturers.

2.2.1 Azodicarbonamide

One of the most common and popular CBA would be azodicarbonamide (ADC) which consist of almost 85% (Kirk-Othmer, 2005) of total CBA used in producing

cellular polymer. ADC is favored due to some of its characteristics such as high gas yield, low toxicity of ADC and decomposition products, giving stable dimensions and properties of foam after manufacture and the ability to tailor the decomposition temperature by addition of suitable activators (Sims & Jaafar, 1994; Sims & O'Connor, 1997).

ADC decomposes to produce mainly nitrogen with lesser amount of carbon monoxide, carbon dioxide and ammonia (Annicelli, 2001). Nitrogen, which is an inert gas, has slow rate of diffusion through polymers and hence makes it a very efficient gas for expanding most polymers.

There are also disadvantages on using ADC as blowing agent. One of them would be the highly exothermic decomposition of ADC which will result in heat build-up of the polymers especially in thick section and ultimately causing reduction in foam mechanical properties (Sims & O'Connor, 1997).

Another disadvantage of ADC is the inconsistency in processes and may result in variable product quality, although the processing of polymer foams using ADC is well established (Jaafar & Sims, 1993a; b). This is due to the complex decomposition mechanism of ADC. Thomas, *et al.* (1993), Thomas & Eastup (1998), Chung (2004) and Hurnik (2009), suggested that the mechanism of decomposition of ADC is complex and still not fully understood until now, where the mechanism may change according to the decomposition environment such as surrounding temperature and medium. Chung (2004) stated that the processing temperature not only influence the rate of decomposition, but may also change the decomposition pathway. ADC is having a number of decomposition reactions and further decomposition reactions of unstable intermediates (Sims & O'Connor, 1997). In studying of the decomposition of ADC,

Jaafar & Sims (1993b) summarized several reported decomposition pathways of ADC (Figure 2.3) but actual conditions which will lead to certain pathway were not given.

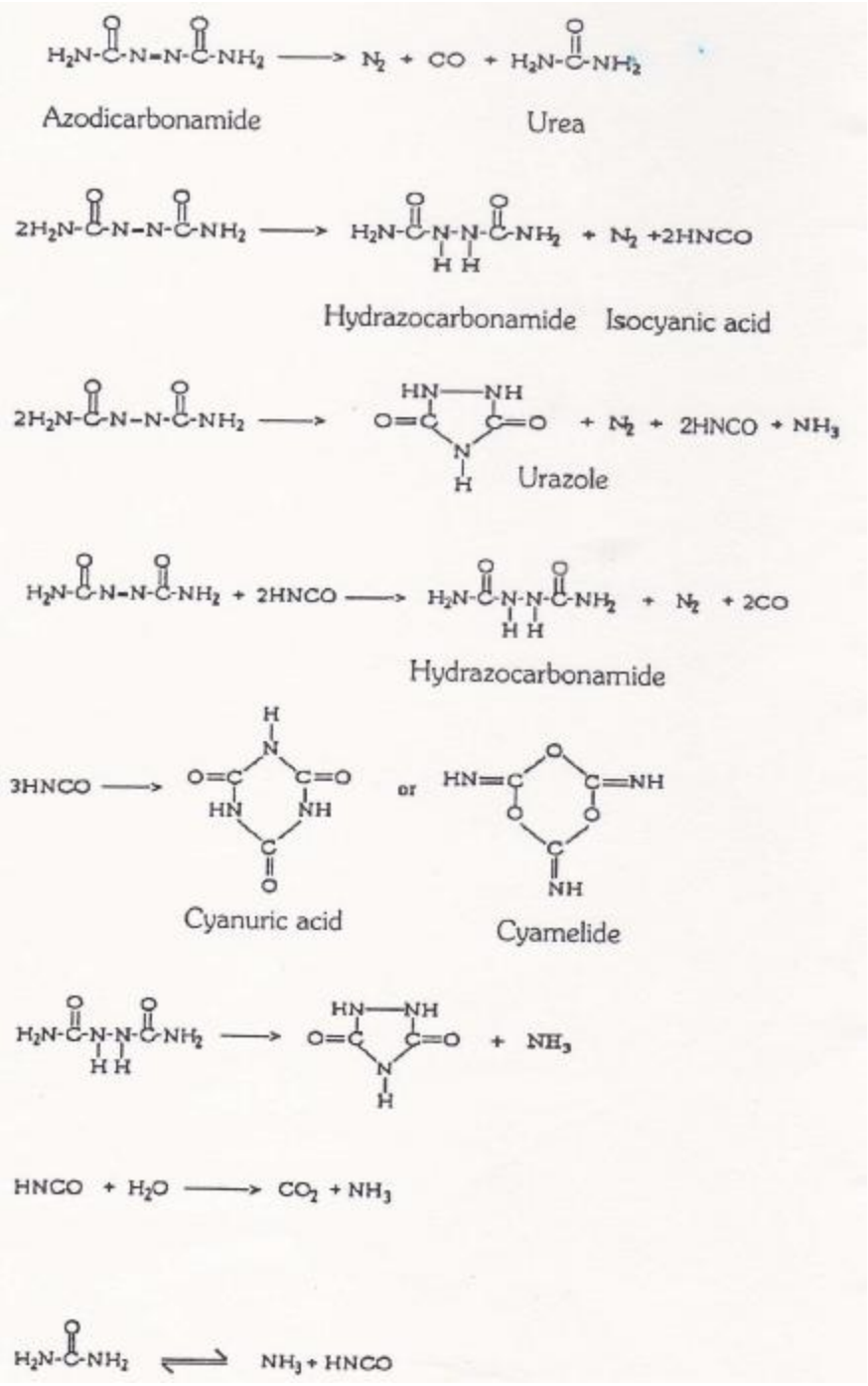

Figure 2.3: Decomposition reactions of ADC (Jaafar & Sims, 1993b, p.305).

Decomposition of ADC can both be activated and deactivated by different additives (Jaafar & Sims, 1993a). In this research, only activation of ADC is given

attention as this will lead to ease of processing. Pure ADC has a decomposition temperature in the range of 190 – 240^{o}C, where different ranges were reported by different works. The temperature range of ADC decomposition leads it somehow not useful in processing of cellular polymer especially for some heat sensitive polymer such as polyvinyl chloride (PVC). The decomposition of ADC can be activated and the decomposition temperature can be modified to a range of 150 – 210^{o}C by a variety of materials based on group 12 and group 14 metal salts, primarily lead oxide, zinc oxide, zinc stearate and zinc acetate (Jaafar & Sims, 1993b). Sims & Jaafar (1994) reported that 4,4'-oxybis(benzenesulphonylhydrazide) (OBSH) added as co-blowing agent can also activate the decomposition of ADC in the sense that the heat generated by exothermic decomposition of high concentration of OBSH is sufficient to activate the ADC at a much lower temperature. The degree of reduction of decomposition temperature will depends on the kind and amount of additives used.

Although it is established that usage of ADC in conjunction with activators will reduce the decomposition temperature of ADC, but the work of Sombatsompop & Lertkamolsin (2000) showed that ADC may not be completely decomposed at 170^{o}C even with activators added. They tried to produce NR foams at temperature of 170^{o}C by incorporating ADC and OBSH as blowing agents to compare the results. Although 4 parts per hundred rubber (pphr) of ZnO and 2 pphr of stearic acid were added as activator in producing NR foams, the density of foams foamed by ADC is higher than the foams produced by OBSH. The results were in disagreement with theoretical prediction as the gas yield of ADC and OBSH are 220 cm^3/g and 125 cm^3/g respectively (Rosato, *et al.*, 2004). Based on the gas yield of both blowing agents, it is predicted that ADC should produce lower density foam than OBSH. The deviation of practical result

of Sombatsompop & Lertkamolsin (2000) from theory can be explained by the incomplete decomposition of ADC in their research.

2.2.2 Water as Physical Blowing Agent

Water is normally used as blowing agent in blowing PU foam, either rigid or flexible foam as shown by works of many researchers (Fanney & Zarr, 1999; Kim & Youn, 2000; Niyogi, *et al.*, 2004; Murayama, *et al.*, 2005). In those researchers, water was treated as CBA where the reaction of water with isocyanate produces carbon dioxide and the gas will act as the actual blowing agent to form PU foam. Polyisocyanate is one of the monomers together with polyol which can be polymerized into PU.

$$R - NCO + H_2O \rightarrow R - NHCOOH \rightarrow R - NH_2 + CO_2 \qquad (2.1)$$

Other than acting as CBA in the production of PU foams, water is actually a potential PBA which can be used to produce cellular polymers. For instance, starch foams are produced by melting and mixing the starch with water which act as a PBA. The water will turn into steam when the system is heated and form air bubbles within the starch matrix (Sivertsen, 2007). Compared to common PBA, water may seem to be an unlikely blowing agent for polymers due to its low volatility and low solubility (Rosato, *et al.*, 2004). Although water is not considered as a volatile material due to relatively low vapor pressure at room temperature, the vapor pressure of water can be increased by increment of temperature and it is stated by Polevoy (1996) that the vapor pressure of water changes very sharply with change in temperature, which is supported by illustration of water vapor pressure versus temperature as shown in Figure 2.4.

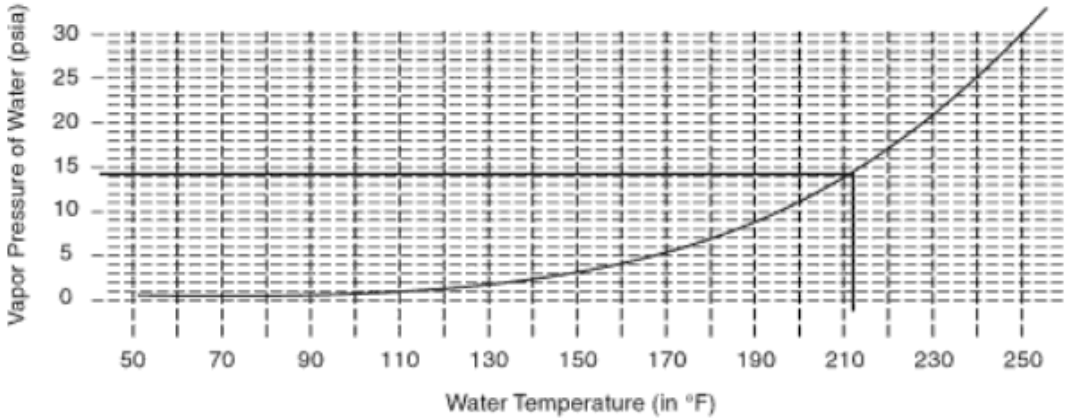

Figure 2.4: Water vapor pressure vs. temperature graph (Johnson, *et al.*, 2008, p.303).

Typical polymer processing temperature, thermoset or thermoplastic, generally is higher than the boiling point of water, 100^{o}C, hence it is highly possible that water can be used as PBA in polymer foam production, although it is not a popular practice in current situation. Manufacturers have started to realize the benefits of using water as PBA, in terms of cost, storage, handling and environmental (Rosato, *et al.*, 2004). Water blown system gives higher production rate opportunities and the cellular polymers produced are recyclable as no impurities from CBA decomposition or residue PBA are present in the polymer matrix.

2.3 Vulcanization and Foam Stabilization

Normally elastomers need to be vulcanized for better properties. Without vulcanization, NR will be having thermoplastic behavior where it will be melted at high temperature and the polyisoprene chains will slip past each other, giving NR the ability to flow and deform permanently under stress. To (2001a) defined vulcanization as a chemical process designed to reduce the effects of heat, cold or solvents on the properties of a rubber compound and to create useful mechanical properties.

Vulcanization introduces crosslinks in the rubber chains and turns plastic and moldable raw rubber into flexible and elastic material named vulcanizate (Ciullo & Hewitt, 1999).

Elastomers can be vulcanized using a few systems depending on the final properties desired and the type of elastomer to be vulcanized. Sulphur vulcanizing system is most commonly used to vulcanize unsaturated elastomers, while saturated elastomers will normally be vulcanized by peroxides. Although carbon–carbon crosslinks are more thermally stable, but the tensile and tear strength are quite poor (Ciullo & Hewitt, 1999).

Sulphur vulcanizing system, depending on the sulphur to accelerator ratio, can result in different properties of vulcanizate (To, 2001a). CV system with high sulphur to accelerator ratio will produce longer polysulphidic linkages, which give rise to better mechanical properties but lower thermal stability, while EV system with low sulphur to accelerator ratio introduces monosulphidic and disulphidic linkages, providing higher thermal stability but lower mechanical strength. An intermediate between the two, called semi-EV system can be used to have both moderate thermal stability and mechanical properties (Nagdi, 1993).

The cure reaction and blow reaction of a rubber compound should be balanced to achieve proper cellular structure. If the two are not balanced, unacceptable cell size of structure may result (Dick, 2001). Cell structure is the result of the interaction between the rate of curing with the evolution of gas (Annicelli, 2011). Faster decomposition of blowing agent may need a faster cure rate to capture the gas as it is released. The only problem is that there is no standard available for the evaluation of blow reaction from blowing agent.

Bascom (1964, cited in Saunders & Klempner, 2004) described the relationships between temperature, viscosity, decomposition temperature of the blowing agent and whether open-cell or closed-cell will be produced. During vulcanization, the viscosity of elastomer will decrease at first as the temperature increases and will increase when the vulcanization starts. Open-cell will be produced if the decomposition of blowing agent occurs before the minimum viscosity, which is the scorch time, because the expansion will occur rapidly, the low viscosity matrix is unable to hold the bubbles and the membranes will rupture before the crosslinks stabilize them. When the blowing agent decomposes after the viscosity of rubber rises, the cell membranes is cured and having sufficient strength to maintain the cell structure without rupture, producing closed-cell foam. Annicelli (2001) added a point that when the cure rate and blow rate is balanced, a very fine cell structure can be obtained.

2.4 Foaming Process

Most plastic processing methods can be used to produce cellular polymer. Cellular polymer can be extruded, injection molded and casted just like bulk polymer, although some adjustment or alteration may need to be done onto the machinery. For research purposes, normally compression molding will be used to produce cellular polymer specimens as compression molding is relatively simple as a polymer processing method and components with complex profile are not necessary in research field. For compression molding in producing cellular polymer, it is generally characterized into two groups, single stage and two-stage foaming, both with their own pros and cons.

2.4.1 Single Stage Foaming

Single stage foaming is conducted by compressing a polymer compound with crosslinking agent, blowing agent and other additives, and foamed and cured under elevated temperature for a period of time. The curing and decomposition of blowing agent is ensured to be completed before the mold is opened rapidly and the foamed polymer will jump out from the mold cavity upon releasing of pressure (Sims & Khunniteekool, 1995; Eaves, 2001; 2004). While having the advantage of simple procedure and short processing time, single stage foaming is having shortcomings such as the mold design is critical to avoid excessive internal stresses, which results in splitting of the foam during expansion and the foam density of less than 70 kg/m^3 cannot be achieved since the rapid rate and high degree of expansion will cause foam splitting (Eaves, 2001; 2004).

By definition, microwave foaming can be categorized into single stage foaming as only one process is involved in the production of rubber foam. The rubber compound is loaded directly into a microwave oven and both vulcanization and blowing are done simultaneously by the application of microwave radiation.

2.4.2 Two-stage Foaming

Tendency to use two-stage foaming process can be seen in past researches as shown in the works of Ariff, *et al.* (2007), Zakaria, *et al.* (2007) and Najib, *et al.* (2011). This may due to the fact that two-stage foaming is having less problem than single stage foaming and research can be done smoothly without the troubles of solving the existing problems of single stage foaming. Two-stage foaming involves compression molding of the rubber compound at low temperature for a short amount of time and after that the procured compound is transferred to hot air oven to foam and vulcanize simultaneously,

hence the phrase “two-stage” comes into the picture. During the first stage, when the mold is opened, the polymer will have little or no expansion due to incomplete or no decomposition of the blowing agent. The polymer is then transferred to hot air oven and the foaming and curing process is completed under elevated temperature (second stage). There is one variant, where high molding temperature is used in the first stage, curing and decomposition of blowing agent are done completely, but the mold is cooled down to ambient temperature before opening. In this case, the polymer will not expand due to high melt strength at lower temperature, and the further expansion is done separately in hot air oven. This variant is also called heat and chill process (Sims & Khunniteekool, 1995).

2.5 Microwave Heating

The word “microwave” is a descriptive term used to identify electromagnetic waves in the frequency spectrum ranging approximately from 300 MHz to 300 GHz. Since the nature of microwave is electromagnetic wave, they are considered to be a flow of photons in quantum physics and the energy of the microwave can be calculated by:

$$E = hf \tag{2.2}$$

where, E = energy of electromagnetic wave

h = Planck’s constant, 4.14×10^{-15} eV.s

f = frequency of the wave

By referring to the frequency range of microwave, it can be calculated that a single microwave photon is having energy ranging from 1.24×10^{-6} to 1.24×10^{-3} eV. Hence, a microwave photon has insufficient energy to break a chemical link as the energy of a molecular bong is larger by several orders of magnitude (Gardiol, 1984). Thus, microwave is a non-ionizing form of radiation. Higher frequency electromagnetic

waves such as ultraviolet, X-ray and gamma-ray are considered ionizing as a single photon from these radiations can have enough energy to extract an electron from an atom and results in ionization.

Microwave as any other forms of electromagnetic waves, can be used in heating of materials as one of the interactions of electromagnetic waves with matter is heating (Gupta, 1979). Chabinsky (1985, cited in Bhowmick & Mangaraj, 1994) stated that in general, conducting materials reflect microwave and insulators transmit them; while dielectric materials like polymer and water absorb microwave energy. Microwave will heat dielectric materials by dielectric heating, where polar molecules are brought into vibration and produce heat.

When microwave radiation is applied onto a material, the molecules of the material will align themselves according to the electromagnetic field if they have induced or permanent dipole moment. Electromagnetic waves are oscillating waves; hence polar molecules with dipole moment will vibrate according to the frequency of the electromagnetic waves and the vibration of molecules leads to molecular friction which cause temperature rise (Indian Rubber Institute, 2000).

Another explanation is that at high frequency of electromagnetic waves, the polar molecules fail to keep in phase with the electric field; hence a portion of energy from the dielectric constant is converted into very fast, kinetic energy, which results in generation of heat (Bhowmick & Managraj, 1994). The total dielectric constant of a material is given by:

$$k_{total} = k_{electronic} + k_{vibration} + k_{orientation} \qquad (2.3)$$

where, k_{total} = dielectric constant of the material

$k_{electronic}$ = dielectric due to movement of electron in a covalent bond

$k_{vibration}$ = dielectric due to displacement of nuclei from its equilibrium position

$k_{orientation}$ = dielectric due to rotation and alignment of whole molecule

and each factor contributing to the dielectric constant will respond to electric field as shown in Figure 2.5. At higher frequency of alternating electric field, relatively large molecules are unable to rotate in phase with the electric field; hence some portion of $k_{orientation}$ is lost and converted into heat. By this theory, it can be predicted that microwave heating will be more effective at higher frequency, and this prediction is supported by the mathematical equation calculating the power absorbed, P by a particular material under microwave radiation:

$$P = 2\pi f \varepsilon_o |E|^2 \varepsilon_r \tan \delta \qquad (2.4)$$

where, ε_o = vacuum permittivity

ε_r = relative permittivity of that material

$tan\ \delta$ = loss tangent

which shows that the power absorbed is directly proportional to the frequency of the electric field.

The advantage of microwave heating is that the object is heated quickly, provided it has sufficient polarity, and uniformly throughout the profile, especially for thick section or profiles with varying thickness (Johnson, 2001). Compared with hot air or infrared heating, where heat is generated outside of the object then transferred towards inside via conduction only, microwave heating generated heat in a distributed manner inside of the material to be treated, allowing a more uniform and faster heating (Gardiol, 1984). Another distinctive aspect of microwave heating is that the surface of

heated object is cooler than the inner part since the surface is in contact with the cold surrounding air.

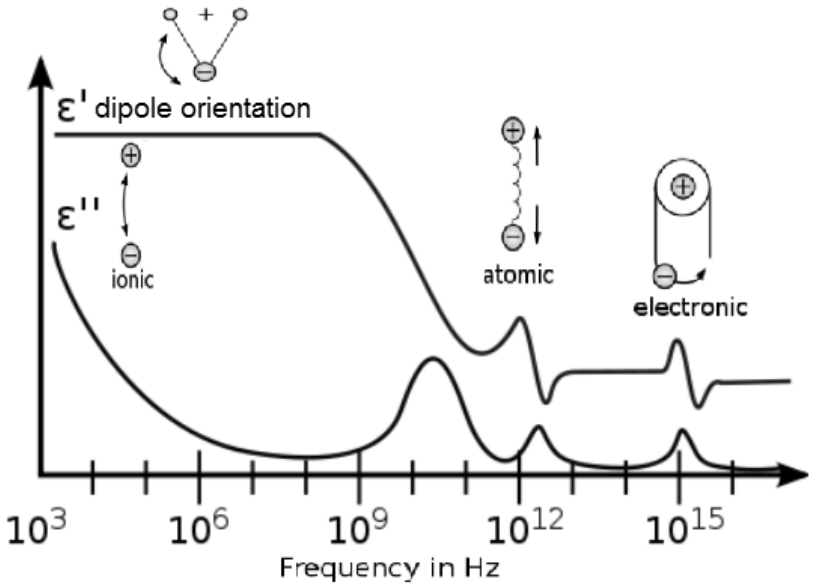

Figure 2.5: Respond of molecules under electric field and the corresponding dielectric properties (modified from Ahmad, 2012, p.8).

The heating effect of microwave leads to many applications in the industrial, scientific and medical (ISM) field. Industrial wise, high power microwave, up to 5 kW, were used for meat tempting, bacon cooking, curing of rubber tires and many other applications (Osepchuck, 2005). In the medical field, microwave can be used in hyperthermia therapy, where the body parts are heated with controlled dosage of microwave in cancer treatment (Gardiol, 1984).

Indian Rubber Institute (2000) stated that nitrogen, oxygen, halogen or sulphur containing rubbers such as acrylonitrile butadiene rubber (NBR), chloroprene rubber (CR) and polyurethane are suitable for microwave curing. NR, although is a nonpolar material, can be made susceptible to microwave heating by adding fillers or additives which are polar in nature. Carbon black, silica, zinc oxide, stearic acid, accelerators and

antioxidants provide microwave absorption and heating capacity to nonpolar rubber compounds (Bhowmick & Mangaraj, 1994). By incorporating mentioned additives into NR, it is believed that the NR compound can be heated under microwave radiation and the temperature rise will be sufficient to cause vulcanization and foaming in the rubber compound and produced cellular NR foam. As mentioned, microwave is non-ionizing; hence the vulcanization is not triggered by the microwave, but is triggered by the heat provided in conjunction with temperature rise of the compound.

2.5.1 Microwave Foaming

In conjunction with microwave heating, the foaming process to produce rubber foam under microwave radiation can also be trigger with the temperature rise of the rubber compound. Since microwave is non-ionizing electromagnetic waves (Gardiol, 1984), the foaming process (decomposition of ADC) is not trigger by the microwave directly, but is contributed by the heat energy applied due to temperature rise of the rubber compound. There is also possibility that the decomposition of ADC can occur before the temperature of rubber compound reaches the onset temperature of ADC decomposition. This is predicted by the fact that ADC is having much polar bonding in the molecule and can be highly susceptible to microwave heating. The onset of decomposition of ADC will be faster in the sense that the ADC molecules will be heated to higher temperature if compared to the bulk rubber compound and the decomposition will occur even before the temperature of bulk rubber compound reaches the mentioned temperature. The molecular structure of ADC can be seen in Figure 2.3.

2.5.2 Penetration Depth

Penetration depth is the depth which microwave can penetrate into matter. Different matter will give different response under microwave radiation (Chabinsky,